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(54) **CATALYST FOR PRODUCING HYDROGEN OR SYNTHESIS GAS AND METHOD OF PRODUCING HYDROGEN OR SYNTHESIS GAS**

(57) This invention provides a catalyst for producing hydrogen gas from a mixed gas comprising dimethyl ether and water vapor or carbon dioxide gas, which comprises copper, iron, cobalt, palladium, iridium, platinum, rhodium, or nickel as an active component, and a method of producing synthesis gas or hydrogen gas in a high yield at a low temperature. By using the catalyst, fuel cell, electricity generation, reduction of iron ore and the like can be carried out.

EP 0 978 314 A1

Description

Technical Field

- 5 [0001] The invention relates to a catalyst for producing hydrogen or synthesis gas from a mixed gas containing dimethyl ether and water vapor or carbon dioxide, and a manufacturing method of hydrogen or synthesis gas using the same.

Background Art

- 10 [0002] Synthesis gas is composed of carbon monoxide and hydrogen, and has wide applications as a raw material for ammonia synthesis and various chemical products, as well as used directly as a raw material for methanol synthesis, oxo synthesis, Fischer-Tropsch synthesis and the like.
- [0003] Heretofore, some methods of manufacturing synthesis gas and methods of manufacturing hydrogen utilizing them are known.
- 15 [0004] For example, there are (1) gasification of coal, (2) steam reforming of hydrocarbon using natural gas, LPG, naphtha or the like as the raw material, (3) partial oxidation of hydrocarbon using natural gas, LPG, naphtha, heavy-duty oil or the like as the raw material, and so on.
- [0005] However, the above coal gasification of (1) has a problem that a very complex and expensive coal gasification oven is necessary, and the apparatus becomes a large scale plant. The steam reforming of hydrocarbon of (2) has a problem that a special reforming oven is necessary because of requiring a high temperature of 700 to 1200 °C for reaction proceeding due to its great endothermic reaction, and the catalyst to be used is required to have a high heat resistance. The partial oxidation of hydrocarbon of (3) has a problem that a special partial oxidation oven is necessary because of requiring a high temperature of 1200 to 1500 °C, the treatment of a large quantity of soot generated with reaction proceeding is a problem, and in the case of using a catalyst, the catalyst is deteriorated by the deposition of a large quantity of carbonaceous material on the surface of the catalyst.
- 20 [0006] An object of the invention is to provide a catalyst and a manufacturing method capable of solving the problems of the above prior art, and obtaining hydrogen or synthesis gas in a high yield at a low temperature.

Disclosure of Invention

- 30 [0007] The inventors investigated eagerly in order to solve the above problems, and as a result, they noted dimethyl ether as the raw material gas. Then, they found that copper, iron, cobalt, palladium, iridium, platinum, rhodium and nickel are very effective as a catalyst for reacting dimethyl ether with water vapor or carbon dioxide to produce hydrogen or synthesis gas, and can produce hydrogen or synthesis gas efficiently at a low temperature to complete the invention.
- 35 [0008] Thus, the invention relates to a catalyst for producing hydrogen gas from a mixed gas comprising dimethyl ether and water vapor or carbon dioxide gas, which comprises copper, iron, cobalt, palladium, iridium, platinum, rhodium, or nickel as an active component, and a method of producing hydrogen or synthesis gas which comprises contacting a mixed gas comprising dimethyl ether and water vapor or carbon dioxide gas with the above catalyst.

40 Brief Description of Drawings

[0009]

- 45 Figure 1 illustrates a constitution of a fuel cell provided with a reformer using the catalyst of the invention.
- Figure 2 illustrates a constitution of a solid electrolyte-type fuel cell using dimethyl ether or hydrogen.
- Figure 3 shows electricity generation characteristics of the solid electrolyte-type fuel cell using dimethyl ether or hydrogen.
- Figure 4 is a flow sheet illustrating an engine electricity generation system using hydrogen or synthesis gas obtained by using the catalyst of the invention.
- 50 Figure 5 is a flow sheet illustrating a general constitution of iron ore reducing system using hydrogen or synthesis gas obtained by using the catalyst of the invention.

- | | |
|------|----------------------------------|
| 1 | Fuel cell |
| 2 | Solid electrolyte-type fuel cell |
| 55 3 | Air supply line |
| 4 | Dimethyl ether supply line |
| 5 | Water vapor supply line |
| 6 | Reformer (reforming reactor) |

11	Sintering machine exhaust gas cooler
12, 13, 14	Heat exchanger
15	Reformer
16	Combustor
5 17	Compressor
18	Gas turbine
19	Electricity generator
20	Heat recovering boiler
21	Heat exchanger
10 22	Blower
23	Reformer
24	Heating furnace
25	Iron ore reducing furnace

15 Best Mode for Carrying Out the Invention

[0010] The catalyst of the invention is able to produce hydrogen gas from a mixed gas comprising dimethyl ether and water vapor or carbon dioxide, and comprises copper, iron, cobalt, palladium, iridium, platinum, rhodium or nickel as an active component.

20 [0011] Among the active components, cobalt, palladium, iridium, platinum, rhodium and nickel produce synthesis gas from dimethyl ether and water vapor, and copper, cobalt and palladium produce synthesis gas from dimethyl ether and carbon dioxide. That is, cobalt and palladium can produce synthesis gas from both of water vapor and carbon dioxide. On the other hand, copper and iron produce mainly hydrogen when using water vapor.

[0012] The active component is incorporated in the catalyst in a form of metal or compound. Preferable copper compounds are copper oxides, and the copper oxides are cuprous oxide (Cu_2O), cupric oxide (CuO) and their mixtures. Preferable iron compounds are iron oxides, and the iron oxides are ferrous oxide (FeO), ferric oxide (Fe_2O_3) and their mixtures. Preferable cobalt compounds are cobalt oxides, and the cobalt oxides are cobaltous oxide (CoO), cobaltic oxide (Co_2O_3) and their mixtures. Preferable palladium compounds are palladium oxides and chlorides, the palladium oxides are palladous oxide (PdO), palladium sesquioxide (Pd_2O_3), palladic oxide (PdO_2), and their mixtures, and the 30 palladium chlorides are palladium dichloride (PdCl_2), palladium tetrachloride (PdCl_4) and their mixtures. Preferable iridium compounds are iridium oxide and chloride, the iridium oxide is IrO_2 , and the iridium chloride is IrCl_3 . Preferable platinum compounds are platinum oxides and chlorides. The platinum oxides are PtO and PtO_2 , and the platinum chlorides are PtCl_2 , PtCl_3 and PtCl_4 . Preferable rhodium compounds are rhodium oxide and chloride. The rhodium oxide is Rh_2O_3 , and the chloride is RhCl_3 . Preferable nickel compounds are nickel sulfides, and the nickel sulfides are NiS , 35 Ni_3S_2 or their mixtures.

[0013] The catalyst of the invention may be carried by a catalyst carrier. Preferable catalyst carriers are oxides, such as alumina, silica gel, silica-alumina, zeolite, titania, zirconia, zinc oxide, tin oxide, lanthanum oxide and cerium oxide, and particularly, alumina is preferable because of high synthesis gas yield. The content in the catalyst is, in the case of copper, about 1 to 50 wt. %, preferably about 3 to 30 wt. %, in the case of iron, about 10 to 100 wt. %, preferably about 40 30 to 100 wt. %, in the case of cobalt, about 1 to 30 wt. %, preferably about 3 to 15 wt. %, in the case of iridium, platinum and rhodium, about 0.05 to 10 wt. %, preferably about 0.1 to 5 wt. %, and in the case of nickel, about 0.5 to 30 wt. %, preferably about 1 to 15 wt. %. When the content is out of the above range, the yield of hydrogen and synthesis gas is degraded.

[0014] The catalyst of the invention may be combined with other metals or compounds than the above metals or their compounds. Examples of the other metals and compounds are, in the case of copper catalyst, zinc, chromium, nickel, manganese, tin, cerium, lanthanum and their compounds. The content of the above third component is 70 wt. % or less, particularly 50 wt. % or less, and in the case of incorporating, in general, about 1 to 30 wt. %.

[0015] In the case of iron catalyst, examples of the other metals and compounds are zinc, nickel, chromium, manganese, tin, cerium, lanthanum and their compounds. Among them, oxides of zinc, nickel, chromium and manganese are preferred. The content of the above third component is 50 wt. % or less, particularly 30 wt. % or less, and in the case of incorporating, in general, about 1 to 20 wt. %. In the case of cobalt catalyst, examples of the other metals and compounds are metals of nickel and iron and their compounds. The content of the above third component is 20 wt. % or less, particularly 10 wt. % or less, and in the case of incorporating, in general, about 1 to 5 wt. %.

[0016] In the case of iridium catalyst, platinum catalyst and rhodium catalyst, examples of the other metals and compounds are metals of copper, cobalt, nickel and iron and their compounds. The content of the above third component is 20 wt. % or less, particularly 10 wt. % or less, and in the case of incorporating, in general, about 1 to 5 wt. %.

[0017] In the case of nickel catalyst, examples of the other metals and compounds are metals and/or compounds of copper, cobalt and iron. The content of the above third component is 20 wt. % or less, particularly 10 wt. % or less, and

in the case of incorporating, in general, about 1 to 5 wt. %.

[0018] The above third components may be incorporated as a single material, or two or more types thereof may be mixed and incorporated.

[0019] It is preferable that the palladium catalyst is carried by a metal oxide having basicity. The metal oxide having basicity is alkali metal oxide, such as Li_2O , Na_2O , K_2O , Rb_2O or Cs_2O , alkaline earth metal oxide, such as BeO , MgO , CaO , SrO or BaO , rare earth element oxide, such as Y_2O_3 , La_2O_3 or CeO_2 , ZnO , SnO_2 , ZrO_2 , Al_2O_3 , TiO_2 and a mixture of two or more of the above metal oxides. The metal oxide having basicity may be combined with another metal oxide not having basicity, such as silica gel, or another compound not having basicity, such as silicon carbide or activated carbon. The carrying rate of palladium is about 0.1 to 30 wt. %, preferably 0.2 to 20 wt. % of the metal oxide having basicity. When the carrying rate of palladium is less than about 0.1 wt. % or more than about 30 wt. %, the yield of synthesis gas is degraded.

[0020] By using the metal oxide having basicity as the carrier of palladium which is an active component, synthesis gas can be produced in a high yield with restraining the production of hydrocarbons mainly methane.

[0021] It is also effective to combine a solid acidic compound with the palladium-carried metal oxide, and by using the catalyst, synthesis gas can be produced from dimethyl ether and water vapor. The catalyst is made by mixing physically palladium carried by the metal oxide and a compound having solid acidity.

[0022] The metal oxide used for carrying palladium is silica gel, titania, alumina, silica - alumina, zirconia, tin oxide, zinc oxide or the like, and particularly, silica gel and titania are preferable because of high synthesis gas yield. The palladium carried by the metal oxide is about 0.05 to 30 wt. %, preferably about 0.1 to 20 wt. % of the metal oxide. When the carrying rate of palladium is less than about 0.05 wt. % or more than about 30 wt. %, the yield of synthesis gas is degraded. To one side of the catalyst components constituting the catalyst of the invention, other metal(s) than palladium or compound(s) thereof can be combined. Examples of the other metal(s) and compound(s) are alkali metal oxides, such as Li_2O , Na_2O , K_2O , Rb_2O and Cs_2O , alkaline earth metal oxides, such as BeO , MgO , CaO , SrO and BaO , rare earth element oxides, such as Y_2O_3 , La_2O_3 and CeO_2 , and mixtures of two or more of the above metal oxides. The content of the above third component is 20 wt. % or less, particularly 10 wt. % or less, and in the case of incorporating, in general, about 1 to 5 wt. %.

[0023] The compounds having solid acidity are alumina, silica - alumina, silica - titania, zeolite, aluminum phosphate and the like, and alumina is particularly preferred because of high synthesis gas yield.

[0024] In the catalysis, by the catalytic action of the compound having solid acidity, dimethyl ether is hydrolyzed to produce methanol (formula (1)), and subsequently, produced methanol is contacted with palladium-carried metal oxide catalyst to produce synthesis gas by decomposing the methanol (formula(2)). By mixing the above two types of catalysts physically, synthesis gas can be obtained in a high yield.



[0025] To the production of the above respective catalysts, general preparations of these type catalysts can be applied. For example, an inorganic acid salt, such as nitrate, carbonate or halide, or an organic acid salt, such as acetate or oxalate, as the compound of the catalytic activity component metal can be used as the raw material for producing the catalyst. For the carrying operation of the active component onto the catalyst carrier, usual techniques, such as precipitation, kneading, impregnation and ion-exchange method, can be utilized. The catalyst composition thus produced is optionally sintered by a conventional method. The sintering is preferably conducted by heating at 300 to 800 °C for 1 to 10 hours in nitrogen or air atmosphere.

[0026] Moreover, the catalyst is preferably activated before subjected to the reaction, and in the case of metal catalyst, it is preferable to treat at 300 to 600 °C for 1 to 10 hours in a hydrogen atmosphere. On the other hand, the previous activation treatment is not necessary for oxide catalysts. In the case of sulfides, it is preferable to treat at 300 to 600 °C for 1 to 10 hours in a hydrogen atmosphere containing 1 to 50 % of hydrogen sulfide (H_2S), dimethyl sulfide (CH_3SCH_3) or dimethyl disulfide (CH_3SSCH_3).

[0027] Upon making nickel into a sulfide, the sulfidation, may be carried out according to a conventional method, and it is preferable to heat at 300 to 600 °C for 1 to 10 hours in an atmosphere of one of hydrogen sulfide, dimethyl sulfide, dimethyl disulfide or carbon disulfide or a mixed gas of two or more of them or a mixed gas of the above and hydrogen. A suitable mixing ratio of hydrogen and the above sulfur compound is about 1:0.05 to 1:1.

[0028] Upon manufacturing a catalyst of palladium carried by a metal oxide having basicity, the basicity of the metal oxide having basicity is lost by contacted with a strongly acidic aqueous solution containing palladium. Thereupon, the manufacturing of the catalyst is characterized by treating with a basic aqueous solution, after palladium is carried by the metal oxide, in order to recover the basicity of the metal oxide. By this treatment, synthesis gas can be obtained in a high yield. That is, it is characterized that, after palladium is carried by the metal oxide having basicity, it is treated with

a basic aqueous solution. As the manufacture of the catalyst, a metal oxide having basicity is added to an aqueous solution containing a metal salt of palladium, such as palladium chloride, evaporated to dryness, dried, followed by sintering. The sintering is preferably carried out by heating at 350 to 600 °C for 1 to 10 hours in nitrogen or air. Subsequently, this matter is treated with basic aqueous solution. As the basic aqueous solution, aqueous solutions of hydroxide or carbonate of alkali metal and hydroxide of alkaline earth metal can be listed. A suitable concentration the basic compound is about 0.5 to 20, usually about 1 to 10. The treatment is carried out by contacting the catalyst with the basic aqueous solution, followed by removing the basic aqueous solution. This treatment is preferably carried out at ordinary temperature to 80 °C for 1 to 5 hours. Besides, it is possible that after treated with basic aqueous solution, for example, a small amount (e.g. about 0.1-1.0) of the above basic compound is carried. The catalyst is activated in the final stage of preparation, and the activation is preferably carried out by treating at 350 to 600 °C for 1 to 10 hours in a hydrogen atmosphere.

[0029] To the production of the palladium-carried metal oxide catalyst in the catalyst containing the palladium-carried metal oxide and the solid acidic compound, general preparations of this type catalyst can be applied. For example, an inorganic acid salt, such as nitrate, carbonate or halide, or an organic acid salt, such as palladium acetate or palladium oxalate, can be used as the palladium compound of the raw material for producing the catalyst. For the carrying operation of palladium onto the metal oxide carrier, usual techniques, such as precipitation, kneading, impregnation and ion-exchange method, can be utilized. The catalyst composition thus produced is optionally sintered by a conventional method. The sintering is preferably conducted by heating at 300 to 600 °C for 1 to 10 hours in nitrogen or air atmosphere. Subsequently, the catalyst composition is preferably treated at 300 to 600 °C for 1 to 10 hours in a hydrogen atmosphere.

[0030] As to the mixing of the palladium-carried metal oxide and the solid acidic compound, either way may be taken, i.e. both components are pelletized and then mixed with each other physically, or both components are pulverized, mixed physically and then, pelletized by compression molding. The mixing ratio of both components is not especially limited, but selected according to the type of each component, reaction conditions and the like. In usual, the ratio is about 1:10 to 10:1, preferably about 1:5 to 5:1, as a weight ratio.

[0031] Hydrogen or synthesis gas can be obtained in a high yield by streaming a mixed gas of dimethyl ether and water vapor or carbon dioxide through each of the above catalyst thus prepared.

[0032] In the invention, water vapor of carbon dioxide is supplied together with dimethyl ether which is the raw material. The supply amount, in the case of water vapor, is enough to the theoretical amount or more, and in the case of producing synthesis gas, the supply amount is 1 to 20 times, preferably 1 to 10 times, molar quantity. On the other hand, in the case of producing hydrogen, the supplied amount is 1 to 30 times, preferably 1 to 20 times, molar quantity. When the supply of water vapor is less than one time molar quantity, high dimethyl ether conversion rate cannot be obtained. The supply exceeding 20 times or 30 times is uneconomical. On the other hand, the supply amount, in the case of carbon dioxide, is 0.8 to 2.0 times, preferably 0.9 to 1.5 times, the molar quantity of dimethyl ether which is the raw material. When the supply of carbon dioxide is less than 0.8 time molar quantity, high dimethyl ether conversion rate cannot be obtained. Exceeding 20 times molar quantity is also undesirable because of the necessity of removing carbon dioxide which remains abundantly in the produced gas. It is a matter of course that carbon dioxide is combined with water vapor. The raw material gas can contain other component(s) than dimethyl ether and water vapor or carbon dioxide. In the case of using carbon dioxide, the molar ratio of H₂ is raised by adding water vapor as the other component.

[0033] Particularly, in the case of the catalyst using cobalt as an active component and of the catalyst of palladium carried by a metal oxide having basicity, water vapor and/or carbon dioxide is supplied together with dimethyl ether which is the raw material. The supply amount in the case of supplying one of water vapor or carbon dioxide is the same as above. On the other hand, in the case of supplying both water vapor and carbon dioxide, the total of water vapor and carbon dioxide is 1 to 10 times, preferably 1 to 5 times, the molar quantity of dimethyl ether. When the total of water vapor and carbon dioxide is less than one time, high dimethyl ether conversion rate cannot be obtained. Exceeding 10 times molar quantity is also undesirable because of uneconomy and the necessity of removing carbon dioxide.

[0034] The raw material gas may contain other component(s) than dimethyl ether and water vapor, carbon dioxide. It can contain inactive gas to the reaction, such as nitrogen, inert gas, CO, H₂ or methane as the other component(s). A suitable content of them is 30 vol. % or less, and exceeding the range induces a problem of decreasing reaction rate. It is desirable to remove air (oxygen) as much as possible because of burning dimethyl ether, and an allowable content is 5 % or less as air.

[0035] The reaction temperature is, in the case of supplying dimethyl ether and water vapor to produce synthesis gas, 200 °C or more, preferably 250 °C or more, particularly preferably 300 °C or more, and 600 °C or less, preferably 500 °C or less, more preferably 450 °C or less, particularly preferably 400 °C or less. In the case of supplying dimethyl ether and carbon dioxide to produce synthesis gas, the reaction temperatures is 200 °C or more, preferably 250 °C or more, particularly preferably 300 °C or more, and 600 °C or less, preferably 500 °C or less, particularly preferably 450 °C or less. In the case of supplying dimethyl ether and water vapor to produce hydrogen, the reaction temperature is 150 °C or more, preferably 200 °C or more, particularly preferably 250 °C or more, and 500 °C or less, preferably 450 °C or

less, particularly preferably 400 °C or less. The catalyst containing copper, platinum or palladium as an active component has a great low temperature activity. In the lower reaction temperature than the above range, high dimethyl ether conversion rate cannot be obtained, and the production rate of carbon dioxide increases to decrease the yield of hydrogen and synthesis gas. In the higher reaction temperature than the above range, in the case of producing synthesis gas, the production of hydrocarbons, mainly methane, is remarkable, and the rate of hydrogen and synthesis gas in the product is decreased, and therefore, undesirable. In the case of producing hydrogen gas, the rate of produced methanol and carbon monoxide as by-products increases in the reaction temperature higher than the above range to decrease the yield of hydrogen. Particularly, in the case of copper catalyst, grain growth of copper which is the active component is remarkable to decrease catalytic activity gradually, and therefore, undesirable.

[0036] The reaction pressure is preferably ordinary pressure to 10 kg/cm². When the reaction pressure exceeds 10 kg/cm², the conversion rate of dimethyl ether decreases.

[0037] A preferable space velocity (supply velocity m³/h of the mixed gas in the standard conditions per 1 m³ catalyst) is, in the case of the production of synthesis gas, 1,000 to 20,000 m³/m³ · h, in the case of the production of hydrogen, 1,000 to 50,000 m³/m³ · h, particularly 30,000 m³/m³ · h or less. When the space velocity is greater than the above range, the conversion rate of dimethyl ether decreases. On the other hand, the space velocity of smaller than the above range is uneconomical, because the size of a reactor is very large.

[0038] In the method of the invention, the apparatus may be either a fixed bed or a fluidized bed.

[0039] In the case of producing synthesis gas by using the catalyst of the invention, as to the cobalt catalyst, the conversion rate of dimethyl ether is about 70 to 100 %, usually about 80 to 100 %, and synthesis gas can be obtained in a yield of about 70 to 100 %, usually about 80 to 95 %. The H₂/CO ratio of the produced synthesis gas is about 0.5 to 4, usually about 0.6 to 3 as molar ratio. As to by-products, methanol is 2 or less, usually 1 or less, and hydrocarbons are 20 or less, usually 10 or less.

[0040] As to the palladium-carried basic metal oxide catalyst, the conversion rate of dimethyl ether is about 60 to 100 %, usually about 80 to 100 %, and synthesis gas can be obtained in a yield of about 60 to 100 %, usually about 80 to 100 %. As to by-products, methanol is 1.0 or less, usually 0.5 or less, and hydrocarbons are 10 or less, usually 5 or less.

[0041] As to the iridium catalyst, the conversion rate of dimethyl ether is about 60 to 100 %, usually about 70 to 100 %, and synthesis gas can be obtained in a yield of about 60 to 95 %, usually about 70 to 95 %. As to by-products, methanol is 10 % or less, usually 5 % or less, and hydrocarbons are 20 % or less, usually 10 % or less.

[0042] As to the platinum catalyst, the conversion rate of dimethyl ether is about 60 to 100 %, usually about 70 to 100 %, and synthesis gas can be obtained in a yield of about 50 to 90 %, usually about 60 to 80 %. As to by-products, methanol is 20 % or less, usually 10 % or less, and hydrocarbons are 5 % or less, usually 5 or less.

[0043] As to the rhodium catalyst, the conversion rate of dimethyl ether is about 50 to 100 %, usually about 60 to 90 %, and synthesis gas can be obtained in a field of about 50 to 90 %, usually about 60 to 80 %. As to by-products, methanol is 10 % or less, usually 5 % or less, and hydrocarbons are 20 % or less, usually 10 % or less.

[0044] As to the catalyst composed of palladium-carried metal oxide and solid acidic compound, the conversion rate of dimethyl ether is about 50 to 100 %, usually about 60 to 100 %, and synthesis gas can be obtained in a yield of about 40 to 90 %, usually about 50 to 90 %. As to by-products, methanol is 20 % or less, usually 5 % or less, and hydrocarbons are 20 % or less, usually 5 % or less.

[0045] As to the nickel catalyst, the conversion rate of dimethyl ether is about 60 to 95 %, usually about 70 to 90 %, and synthesis gas can be obtained in a yield of about 50 to 95 %, usually about 40 to 90 %. As to by-products, methanol is 10 % or less, usually 5 % or less, and hydrocarbons are 20 % or less, usually 5 % or less.

[0046] As to the copper catalyst using carbon dioxide, the conversion rate of dimethyl ether is about 50 to 100 %, usually about 70 to 95 %, and synthesis gas can be obtained in a yield of about 50 to 100 %, usually about 70 to 95 %. The H₂/CO ratio of the produced synthesis gas is about 0.6 to 1.3, usually about 0.8 to 1.1 as molar ratio. As to by-products, hydrocarbons are 5 % or less, usually 2 % or less.

[0047] In the case of producing hydrogen, as to the copper catalyst, the conversion rate of dimethyl ether is about 60 to 100 %, usually about 80 to 100 %, and hydrogen can be obtained in a yield of about 55 to 100 %, usually about 80 to 95 %. As to by-products, methanol is 10 or less, usually 5 or less, hydrocarbons are 0.5 or less, usually 0.3 or less, and carbon monoxide is 10 or less, usually 5 or less.

[0048] As to the iron catalyst, the conversion rate of dimethyl ether is about 80 to 100 %, usually about 90 to 100 %, and hydrogen can be obtained in a yield of about 70 to 100 %, usually about 80 to 100 %. As to by-products, methanol is 0.5 or less, usually 0.3 or less, hydrocarbons are 5 or less, usually 2 or less, and carbon monoxide is 10 or less, usually 5 or less.

[0049] The hydrogen and synthesis gas produced from dimethyl ether using the catalyst of the invention can be used for fuel cell.

[0050] Recently, electricity generation by fuel cell has been noted, because of less environmental pollution, less noise, less energy loss and advantages in setting and operation.

[0051] Since fuel cell is, in principle, an energy converter converting chemical energy of hydrogen which is fuel gas

directly to electric energy, a stable supply in large quantity of hydrogen is necessary. The supply in large quantity of hydrogen is carried out using city gas containing hydrocarbons, such as methane or natural gas, propane, butane or petroleum gas, naphtha, kerosene, gas oil or synthetic petroleum oil or hydrogen, as a principal component, or methanol, as the raw material fuel, and reforming them to hydrogen and carbon dioxide gas or carbon monoxide by a reformer,

[0052] In the case of using the raw material fuel for a portable electric source of an electric car or fuel cell for electricity generation plant located at a far place where city gas cannot be utilized, preferable raw material fuels are liquids and easily liquefiable materials, such as propane, butane, naphtha, kerosene, gas oil, synthetic petroleum oil and methanol, in terms of transportation, storage place, safety and the like. However, in the case of using a heavy-duty hydrocarbon, such as propane, butane, naphtha, kerosene, gas oil or synthetic petroleum oil, there is a problem of decreasing reforming efficiency due to the deposition of carbon on the catalyst surface during reforming, unless setting of reformer conditions is carefully controlled. Methanol containing oxygen has no problem of carbon deposition, but corrosion of reformer is a problem because of producing formic acid exhibiting strong corrosive action in the reforming process.

[0053] On the other hand, a national project is being scheduled, wherein dimethyl ether which is clean, not containing ashes and sulfur, and excellent in handling is mass-produced cheaply from poor grade coals, and utilized for fuel. Dimethyl ether is expected to be utilized for new applications, such as fuel cell, in view of transportation, storage place, safety and the like, and also in view of environmental protection, due to its easy liquefaction by pressuring at several atmospheric pressures.

[0054] Heretofore, to apply dimethyl ether to fuel cell has not been reported yet.

[0055] The inventors investigated whether dimethyl ether can be reformed without a problem as fuel gas by a reformer for reforming conventional raw material fuels for fuel cell to fuel gases or not.

[0056] A comparison of the composition of the reformed gas with natural gas (methane) is shown in Table 1.

[0057] It can be seen that dimethyl ether can be reformed to hydrogen, carbon monoxide and water vapor even using a conventional reformer, similar to natural gas.

[0058] Accordingly, dimethyl ether can be utilized as a raw material for fuel cell without a problem.

Table 1

Raw Material Fuel	H ₂ O	H ₂	CO	Others
Dimethyl ether	27.3	47.6	12.6	12.5
Methane	29.2	51.1	9.1	10.6
Unit ; vol.%				

[0059] In the case of solid electrolyte-type fuel cell, it is already known that the cost of solid electrolyte-type fuel cell is reduced by supplying methane and water vapor as the fuel gas directly to a fuel electrode (anode) to reform in the cell without passing a reformer, due to its high operation temperature of about 1,000 °C. However, electricity generation is also possible without a problem by supplying a mixed gas containing dimethyl ether and water vapor directly as the fuel gas.

[0060] A constitution of a fuel cell provided with a reformer is shown in Figure 1. In the figure, 1 is a fuel cell, 3 is an air supply line, 4 is a dimethyl ether supply line, 5 is a water vapor supply line, and 6 is a reformer, respectively.

[0061] Electricity generation can be conducted by using dimethyl ether as the raw material, supplying it to the reformer 6 together with water vapor to be reformed to hydrogen and carbon monoxide or carbon dioxide, and then, supplying it to the anode of the fuel cell and air which is the oxidizing agent to the cathode of the fuel cell 1.

[0062] A constitution of a solid electrolyte-type fuel cell is shown in Figure 2. In the figure, 2 is a solid electrolyte-type fuel cell.

[0063] When a mixed gas containing dimethyl ether and water vapor is supplied directly to the anode of the solid electrolyte-type fuel cell 2 without passing a reformer, dimethyl ether 4 is reformed at the anode to hydrogen and carbon monoxide or carbon dioxide, etc. due to contacting an electrode material having catalytic action at a high temperature near 1,000 °C. Accordingly, electricity generation can be conducted by supplying air which is the oxidizing agent to the cathode of the solid electrolyte-type fuel cell 2.

[0064] It is no problem that the mixed gas containing dimethyl ether and water vapor contains inactive gas, such as argon.

[0065] Electricity can be generated by reforming dimethyl ether using the catalyst of the invention to produce synthesis gas or hydrogen gas, and using the gas as the fuel for engine.

[0066] Heretofore, some methods of generating electricity using dimethyl ether are known.

[0067] For example, Japanese Patent KOKAI 2-9833 and 3-52835 disclose electricity generation methods of produc-

ing a combination of dimethyl ether and methanol from synthesis gas to store them, and using them in an integrated gasification complex cycle electricity generation plant at the peak of natural gas electricity generation.

[0068] On the other hand, an electricity generation method using methanol reformed gas is known. The method is of obtaining the synthesis gas or hydrogen gas used as a fuel for electricity generation by reforming or cracking of methanol.

[0069] In the methanol reforming electricity generation method, a method of carbureting (increasing heat) is also proposed by utilizing exhaust gas of turbines for electricity generation or combustion exhaust gas for the reforming or cracking which is endothermic reaction. For example, Japanese Patent KOKAI 62-132701 discloses a heat recovering method which utilizes the heat quantity of combustion exhaust gas for heating raw materials. The exhaust gas is of heat medium-heating furnace for supplying heat necessary for reaction proceeding and heating raw material gases to evaporate, in a methanol cracking apparatus for producing synthesis gas from methanol and water.

[0070] However, in the electricity generation method disclosed in Japanese Patent KOKAI 2-9833 and 3-52835, there is no description concerning concrete electricity generation method at all.

[0071] Moreover, in the methanol reforming electricity generation method, the electricity generation efficiency is improved by carbureting (increasing heat) using waste heat of the exhaust gas of turbines for electricity generation or combustion exhaust gas for reforming or cracking of raw material methanol. However, the heat quantity recoverable through steam reforming of methanol and methanol cracking is not so great as shown in the formulas (1) and (2), respectively.



[0072] Besides, there are problems of careful handling and the like, because methanol has toxicity.

[0073] The inventors noted the method of obtaining synthesis gas or hydrogen gas by reforming dimethyl ether which has been developed by the inventors, and devised an electricity generation method using the gas as fuel for engine.

[0074] This method is an electricity generation method using dimethyl ether reformed gas which comprises reforming dimethyl ether to produce synthesis gas or hydrogen gas by adding water vapor or carbon dioxide gas to dimethyl ether followed by catalyzing, and using the gas as a fuel for engine, and uses an electricity generation apparatus comprising a reformer packed with a catalyst for reacting dimethyl ether with water vapor or carbon dioxide gas to produce synthesis gas or hydrogen gas, a combustor for burning the synthesis gas or hydrogen gas, and an electricity generator having gas turbine rotating by the combustion exhaust gas generated in the combustor.

[0075] In the reforming reaction relating to the invention, heat quantity of endothermic reaction is great as shown in the formulas (3)-(5), and accordingly, it is possible to recover waste heat 1.5 to 2.5 times as much as the conventional methanol reforming reaction, and heat quantity upon burning the reformed gas increases by the recovered heat quantity.



[0076] For example, when 1 Nm³ dimethyl ether having a gross calorific value of 15,580 kcal/Nm³ is reformed by water vapor according to the formula (3), a synthesis gas consisting of 2 Nm³ carbon monoxide and 4 Nm³ hydrogen is obtained. The gross calorific value of the synthesis gas is 18,240 kcal, and the increase of heat quantity is 2,660 kcal. The rate of heat quantity increase (the increase of heat quantity is divided by the gross calorific value of dimethyl ether, and multiplied by 100) is calculated 17.1 %. On the other hand, in the methanol reforming reaction, when 1 Nm³ methanol vapor having a gross calorific value of 8,150 kcal/Nm³ is cracked, for example, according to the formula (2), a synthesis gas consisting of 1 Nm³ carbon monoxide and 2 Nm³ hydrogen is obtained. The gross calorific value of the synthesis gas is 9,120 kcal, and the increase of heat quantity is 970 kcal. The rate of heat quantity increase (the increase of heat quantity is divided by the gross calorific value of dimethyl ether, and multiplied by 100) is calculated 11.9 %.

[0077] Besides, dimethyl ether has already been utilized as a propellant for spray, and confirmed that its toxicity is very small compared with methanol.

[0078] In the method of the invention, it is preferable to give the reaction heat necessary for reforming dimethyl ether by the medium, low temperature waste heat at 200 to 500 °C generated in a iron manufacturing factory or an electricity generation plant. For example, by using the sensible heat of the exhaust gas of a cooler generated in a sintering factory

of an iron manufacturing factory, or by utilizing the exhaust gas of gas turbines in an electricity generation plant, an increase of the calorific value corresponding to the heat quantity of the reforming can be promised in the produced reformed gas. Furthermore, the reforming of dimethyl ether proceeds at a temperature of 200 to 500 °C by the presence of the above catalyst, and is suitable for the recovery of medium, low temperature waste heat.

[0079] The reformed gas of dimethyl ether is gaseous fuel comprising mainly hydrogen or hydrogen and carbon monoxide, and is used as a fuel for an engine for electricity generation, such as gas turbine. As the method of combustion, the low temperature combustion, such as catalytic combustion and dilute gas combustion, is also possible as well as normal combustion, and in this case, the retardation of nitrogen oxides generation can be expected.

[0080] The combustion conditions may be similar to the conventional conditions using LNG or LPG.

[0081] Iron ore and recovered scrap iron can be reduced by using synthesis gas or hydrogen gas obtained by reforming dimethyl ether using the catalyst of the invention.

[0082] Heretofore, in the method of manufacturing reduced iron by reducing iron ore, some methods of producing synthesis gas or hydrogen gas which is a reducing gas are known.

[0083] For example, there are (1) gasification of coal, (2) steam reforming of hydrocarbon using natural gas, LPG, naphtha or the like as the raw material, (3) partial oxidation of hydrocarbon using natural gas, LPG, naphtha, heavy-duty oil or the like as the raw material, and so on.

[0084] However, the above coal gasification of (1) has a problem that a very complex and expensive coal gasification oven is necessary, and the apparatus becomes a large scale plant. The steam reforming of hydrocarbon of (2) has a problem that a special reforming oven is necessary because of requiring a high temperature of 700 to 1200 °C for reaction proceeding due to its great endothermic reaction, and the catalyst to be used is required to have a high heat resistance. The partial oxidation of hydrocarbon of (3) has a problem that a special partial oxidation oven is necessary because of requiring a high temperature of 1200 to 1500 °C, the treatment of a large quantity of soot generated with reaction proceeding is a problem, and in the case of using a catalyst, the catalyst is deteriorated by the deposition of a large quantity of carbonaceous material on the surface of the catalyst.

[0085] The inventors devised a method of producing synthesis gas or hydrogen gas by reforming dimethyl ether using the catalyst of the invention, and a method of reducing iron ore and recovered scrap iron using the gas.

[0086] The above method includes a method of manufacturing reduced iron which comprises reforming dimethyl ether to produce synthesis gas or hydrogen gas by adding water vapor or carbon dioxide gas to dimethyl ether followed by catalyzing, and reducing iron ore or recovered scrap iron, a method of manufacturing reduced iron as described above wherein the reforming of dimethyl ether is carried out using an exhaust gas containing water vapor and carbon dioxide gas generated by reducing iron ore or recovered scrap iron, and a method of manufacturing reduced iron as described above wherein the sensible heat of an exhaust gas generated by reducing iron ore or recovered scrap iron for heating the reforming of dimethyl ether, and uses an apparatus for manufacturing reduced iron which comprises a reformer packed with a catalyst for reacting dimethyl ether with water vapor or carbon dioxide gas to produce synthesis gas or hydrogen gas, reducing furnace charged with iron ore or recovered scrap iron, wherein they are connected so as to supply the synthesis gas or hydrogen gas produced in the reformer to the reducing furnace.

[0087] As to the reducing furnace of iron ore or recovered scrap iron, the type is not especially limited, and any known type of shaft type furnace, kiln type furnace, fluidized bed type furnace or rotary kiln type furnace is usable.

[0088] The reducing conditions may be similar to the conventional method, at a temperature of about 800 to 1,000 °C, at a pressure of about 1 to 10 atmospheric pressures, for a period of about 2 to 8 hours.

[0089] In the invention, it is preferable to use the water vapor and carbon dioxide gas contained in the exhaust gas generated by reducing iron ore for a part or the whole of the water vapor or carbon dioxide. The composition of the exhaust gas is about 0 to 5 vol. % of water vapor, about 0 to 5 vol. % of carbon dioxide gas, about 0 to 5 vol. % of nitrogen and about 0 to 1 vol. % of oxygen, and the temperature of the medium, low temperature exhaust gas is about 300 to 500 °C at the exit of the reducing furnace.

Examples

Examples 1-4

[0090] An aqueous solution of 91 g cupric nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), 73 g zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 368 g aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) dissolved in about 2 l demineralized water and an aqueous solution of about 250 g sodium carbonate (Na_2CO_3) dissolved in about 2 l demineralized water were introduced dropwise into a stainless steel container containing about 5 l demineralized water kept at about 80 °C for about 2 hours, while adjusting the pH to 8.0 ± 0.5 . After the introduction, maturing was carried out for about 1 hour with leaving as it is. While, the pH was adjusted to 8.0 ± 0.5 by adding dropwise about 1 mol/l nitric acid aqueous solution or about 1 mol/l sodium carbonate aqueous solution. Subsequently, produced precipitates were filtered, and washed with demineralized water until nitrate ion was not detected in the washed solution. The cake thus obtained was dried at 120 °C for 24 hours, and sintered at 350 °C

for 5 hours in air. Furthermore, the sintered matter was sieved to collect 20 to 40 mesh fractions to obtain the object catalyst.

[0091] The composition of the obtained catalyst was $\text{CuO}:\text{ZnO}:\text{Al}_2\text{O}_3 = 30:20:50$ (weight ratio).

Example 5-8

[0092] A catalyst was prepared according to the same method as Examples 1-4, except that 105 g chromium nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$) was used instead of zinc nitrate.

[0093] The composition of the obtained catalyst was $\text{CuO}:\text{Cr}_2\text{O}_3:\text{Al}_2\text{O}_3 = 30:20:50$ (weight ratio).

Reaction Method

[0094] A prescribed amount of the above catalyst was packed in a stainless steel reaction tube having an inside diameter of 20 mm. A prescribed amount of dimethyl ether and carbon dioxide were supplied to the reaction tube, and the reaction was carried out at a prescribed temperature.

[0095] The reaction products and unreacted materials obtained by the above operations were analyzed by gas chromatography.

Reaction Conditions and Experimental Results

[0096] The reaction conditions and experimental results are shown in Tables 2 and 3.

$$\text{Synthesis gas yield (\%)} = \frac{1/6 \times (\text{CO producing rate} + \text{H}_2 \text{ producing rate})}{\text{Dimethyl ether supply rate}} \times 100$$

$$\text{Hydrocarbon yield (\%)} = \frac{\sum [n/2 \times \text{Hydrocarbon producing rate}]}{\text{Dimethyl ether supply rate}} \times 100$$

n: number of carbon atoms

[0097] All units of each rate are $[\text{mol/g-cat} \cdot \text{h}]$

Table 2

			Example 1	Example 2	Example 3	Example 4
Catalyst (Weight ratio)			CuO-ZnO-Al ₂ O ₃ (30 : 20 : 50)			
Conditions	Temperature (°C)		250	300	350	300
	CO ₂ /Dimethyl Ether (Molar Ratio)		1	1	1	2
	Space Velocity (h ⁻¹)		5000	5000	5000	3000
Results of Reaction	DME Conversion Rate (%)		74.8	78.2	83.1	85.5
	Yield (%)	Synthesis Gas	74.1	76.0	79.8	85.1
		Hydrocarbons	0.7	2.2	3.7	0.4
	H ₂ /CO in Synthesis Gas (Molar Ratio)		0.98	0.92	0.86	0.72

Table 3

			Example 5	Example 6	Example 7	Example 8
Catalyst (Weight ratio)			CuO-ZnO-Al ₂ O ₃ (30 : 20 : 50)			
Conditions	Temperature (°C)		250	300	350	300
	CO ₂ /Dimethyl Ether (Molar Ratio)		1	1	1	2
	Space Velocity (h ⁻¹)		5000	5000	5000	3000
Results of Reaction	DME Conversion Rate (%)		69.3	73.5	77.4	80.7
	Yield (%)	Synthesis Gas	69.0	72.1	75.6	80.6
		Hydrocarbons	0.3	1.4	1.8	0.1
	H ₂ /CO in Synthesis Gas (Molar Ratio)		0.99	0.95	0.91	0.89

DME: Dimethyl ether

Examples 9-11

[0098] An aqueous solution of 91 g cupric nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), 39 g nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 37 g zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 368 g aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) dissolved in about 2 l demineralized water and an aqueous solution of about 200 g sodium hydroxide dissolved in about 2 l demineralized water were introduced dropwise into a stainless steel container containing about 5 l demineralized water kept at about 60 °C for about 1 hours, while adjusting the pH to 8.0 ± 0.5 . After the introduction, maturing was carried out for about 1 hour with leaving as it is. While, the pH was adjusted to 8.0 ± 0.5 by adding dropwise about 1 mol/l nitric acid aqueous solution or about 1 mol/l sodium hydroxide aqueous solution. Subsequently, produced precipitates were filtered, and washed with demineralized water until nitrate ion was not detected in the washed solution. The cake thus obtained was dried at 120 °C for 24 hours, and sintered at 350 °C for 5 hours in air. Furthermore, the sintered matter was sieved to collect 20 to 40 mesh fractions to obtain the object catalyst.

[0099] The composition of the obtained catalyst was $\text{CuO}:\text{NiO}:\text{ZnO}:\text{Al}_2\text{O}_3 = 30:10:10:50$ (weight ratio).

Example 12

[0100] A catalyst was prepared according to the same method as Examples 9-11, except that 53 g chromium nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$) was used instead of nickel nitrate.

[0101] The composition of the obtained catalyst was $\text{CuO}:\text{Cr}_2\text{O}_3:\text{ZnO}:\text{Al}_2\text{O}_3 = 30:10:10:50$ (weight ratio).

Example 13

[0102] A catalyst was prepared according to the same method as Examples 9-11, except that 33 g manganese nitrate ($\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was used instead of nickel nitrate.

[0103] The composition of the obtained catalyst was $\text{CuO}:\text{MnO}_2:\text{ZnO}:\text{Al}_2\text{O}_3 = 30:10:10:50$ (weight ratio).

Example 14

[0104] A catalyst was prepared according to the same method as Examples 9-11, except that 53 g chromium nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$) was used instead of zinc nitrate in Example 13.

[0105] The composition of the obtained catalyst was $\text{CuO}:\text{Cr}_2\text{O}_3:\text{MnO}_2:\text{Al}_2\text{O}_3 = 30:10:10:50$ (weight ratio).

Reaction Method

[0106] A prescribed amount of the above catalyst was packed in a stainless steel reaction tube having an inside diameter of 20 mm. A prescribed amount of dimethyl ether and water vapor were supplied to the reaction tube, and the reaction was carried out at a prescribed temperature.

[0107] The reaction products and unreacted materials obtained by the above operations were analyzed by gas chromatography.

Reaction Conditions and Experimental Results

[0108] The reaction conditions and experimental results are shown in Tables 4 and 5.

$$\text{Hydrogen yield (\%)} = \frac{1/6 \times (\text{H}_2 \text{ producing rate} - 2 \times \text{CO producing rate}) + 1/4 \text{ CO producing rate}}{\text{Dimethyl ether supply rate}} \times 100$$

$$\text{Methanol yield (\%)} = \frac{1/2 \times \text{Methanol producing rate}}{\text{Dimethyl ether supply rate}} \times 100$$

$$\text{CO yield (\%)} = \frac{1/4 \times \text{CO producing rate}}{\text{Dimethyl ether supply rate}} \times 100$$

[0109] All units of each rate are [mol/g-cat · h]

Table 4

		Example 9	Example 10	Example 11
Catalyst (Weight ratio)		CuO-ZnO-Al ₂ O ₃ (30:10:10:50)	CuO-ZnO-Al ₂ O ₃ (30:10:10:50)	CuO-ZnO-Al ₂ O ₃ (30:10:10:50)
Conditions	Temperature (°C)	200	250	300
	CO ₂ /Dimethyl Ether (Molar Ratio)	10	10	10
	Space Velocity (h ⁻¹)	15000	15000	15000
Results of Reaction	DME Conversion Rate (%)		83.3	98.1
	Yield (%)	Hydrogen	79.2	92.0
		Methanol	2.5	3.8
		Hydrocarbons	0.1	0.1
		CO	1.5	2.2

Table 5

		Example 12	Example 13	Example 14
Catalyst (Weight ratio)		CuO-ZnO-Al ₂ O ₃ (30:10:10:50)	CuO-ZnO-Al ₂ O ₃ (30:10:10:50)	CuO-ZnO-Al ₂ O ₃ (30:10:10:50)
Conditions	Temperature (°C)	250	250	250
	CO ₂ /Dimethyl Ether (Molar Ratio)	10	10	10
	Space Velocity (h ⁻¹)	15000	15000	15000
Results of Reaction	DME Conversion Rate (%)		94.3	92.2
	Yield (%)	Hydrogen	86.4	85.1
		Methanol	4.3	4.1
		Hydrocarbons	0.1	0.1
		CO	3.5	2.9

Examples 15-17

[0110] An aqueous solution of 405 g iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), 79 g chromium nitrate ($\text{Cr}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and 37 g aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) dissolved in about 2 l demineralized water and an aqueous solution of about 180 g sodium hydroxide dissolved in about 2 l demineralized water were introduced dropwise into a stainless steel container containing about 5 l demineralized water kept at about 80 °C for about 1 hours, while adjusting the pH to 8.0 ± 0.5 . After the introduction, maturing was carried out for about 1 hour with leaving as it is. While, the pH was adjusted to 8.0 ± 0.5 by adding dropwise about 1 mol/l nitric acid aqueous solution or about 1 mol/l sodium hydroxide aqueous solution. Subsequently, produced precipitates were filtered, and washed with demineralized water until nitrate ion was not detected in the washed solution. The cake thus obtained was dried at 120 °C for 24 hours, and sintered at 350 °C for 5 hours in air. Furthermore, the sintered matter was sieved to collect 20 to 40 mesh fractions to obtain the object catalyst.

[0111] The composition of the obtained catalyst was $\text{Fe}_2\text{O}_3:\text{Cr}_2\text{O}_3:\text{Al}_2\text{O}_3 = 80:15:5$ (weight ratio).

Example 18-20

[0112] A catalyst was prepared according to the same method as Examples 15-17, except that 55 g zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was used instead of chromium nitrate.

[0113] The composition of the obtained catalyst was $\text{CuO}:\text{ZnO}:\text{Al}_2\text{O}_3 = 80:15:5$ (weight ratio).

Reaction Method

[0114] A prescribed amount of the above catalyst was packed in a stainless steel reaction tube having an inside diameter of 20 mm. A prescribed amount of dimethyl ether and water vapor were supplied to the reaction tube, and the reaction was carried out at a prescribed temperature.

[0115] The reaction products and unreacted materials obtained by the above operations were analyzed by gas chromatography.

Reaction Conditions and Experimental Results

[0116] The reaction conditions and experimental results are shown in Tables 6 and 7.

Table 6

		Example 15	Example 16	Example 17
Catalyst (Weight ratio)		$\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ (80:15:5)		
Conditions	Temperature (°C)	300	350	400
	CO_2 /Dimethyl Ether (Molar Ratio)	10	10	10
	Space Velocity (h^{-1})	25000	25000	25000
Results of Reaction	DME Conversion Rate (%)		93.7	100
	Yield (%)	Hydrogen	91.9	95.8
		Methanol	0.1	0.1
		Hydrocarbons	0.2	0.9
		CO	1.5	3.2

Table 7

		Example 18	Example 19	Example 20
Catalyst (Weight ratio)		$\text{Fe}_2\text{O}_3\text{-ZnO-Al}_2\text{O}_3$ (80:15:5)		
Conditions	Temperature (°C)	300	350	400
	CO_2 /Dimethyl Ether (Molar Ratio)	10	10	10
	Space Velocity (h^{-1})	25000	25000	25000
Results of Reaction	DME Conversion Rate (%)		89.1	100
	Yield (%)	Hydrogen	87.6	94.0
		Methanol	0.1	0.1
		Hydrocarbons	0.1	1.3
		CO	1.3	4.6

Examples 21-28

[0117] 49.4 g cobalt acetate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was dissolved in about 300 ml demineralized water, and furthermore, 90 g γ -alumina ("N612", Nikki Kagaku) was put in the aqueous solution, followed by evaporating to dryness. The matter was dried in air at 120 °C for 24 hours, and sintered at 500 °C for 3 hours in air. Subsequently, it was treated in hydrogen current at 500 °C for 3 hours to obtain the catalyst.

[0118] The composition of the obtained catalyst was $\text{Co}:\text{Al}_2\text{O}_3=10:90$ (weight ratio).

Reaction Method

[0119] A prescribed amount of the above catalyst was packed in a stainless steel reaction tube having an inside diameter of 20 mm. A prescribed amount of dimethyl ether and water vapor and/or carbon dioxide were supplied to the reaction tube, and the reaction was carried out at a prescribed temperature.

[0120] The reaction products and unreacted materials obtained by the above operations were analyzed by gas chromatography.

Reaction Conditions and Experimental Results

[0121] The reaction conditions and experimental results are shown in Tables 8 and 9.

$$\text{CO}_2 \text{ yield (\%)} = \frac{1/2 \times \text{CO}_2 \text{ producing rate}}{\text{Dimethyl ether supply rate}} \times 100$$

[0122] All units of each rate are [mol/g-cat · h]

Table 8

		Example 21	Example 22	Example 23	Example 24
Reaction Conditions	Temperature (°C)	250	300	350	400
	H ₂ O/Dimethyl Ether (Molar Ratio)	4	4	4	4
	CO ₂ /Dimethyl Ether (Molar Ratio)	0	0	0	0
	Space Velocity (h ⁻¹)	8000	8000	8000	8000
Results of Reaction	DME Conversion Rate (%)	93.8	100	100	100
	Yield (%)	Synthesis Gas	84.6	91.8	92.0
		Methanol	0.3	0.3	0.5
		Hydrocarbons	0.4	1.1	3.1
		CO ₂	8.5	6.8	4.4
	H ₂ /CO in Synthesis Gas (Molar Ratio)	2.63	2.45	2.36	2.22

Table 9

		Example 25	Example 26	Example 27	Example 28
Reaction Conditions	Temperature (°C)	300	400	500	350
	H ₂ O/Dimethyl Ether (Molar Ratio)	0	0	0	2
	CO ₂ /Dimethyl Ether (Molar Ratio)	1	1	1	0.5
	Space Velocity (h ⁻¹)	5000	5000	5000	5000
Results of Reaction	DME Conversion Rate (%)	83.7	100	100	96.8
	Yield (%)	Synthesis Gas	80.1	88.4	84.1
		Methanol	0	0	0
		Hydrocarbons	3.6	8.9	15.9
		CO ₂	—	—	—
	H ₂ /CO in Synthesis Gas (Molar Ratio)	0.96	0.88	0.61	1.53

Examples 29,30

- [0123] 6 ml hydrochloric acid and 8.33 g palladium chloride (PdCl_2) were dissolved in about 500 ml demineralized water, and 100 g zinc oxide (guaranteed reagent, Kanto Kagaku) was put in the aqueous solution, followed by evaporating to dryness. The matter was dried in air at 120 °C for 24 hours, and further sintered in air at 500 °C for 3 hours. Subsequently, this matter was put in an aqueous solution of 10 g sodium hydroxide dissolved in about 1,000 ml demineralized water, and treated at 50 °C with heating for about 1 hour. Then, it was washed until chloride ion was not detected, and dried at 120 °C for 24 hours. Furthermore, this matter was graded to 20 to 40 mesh by compression molding, and treated in hydrogen current at 500 °C for 3 hours to obtain the catalyst.
- [0124] The composition of the obtained catalyst was $\text{Pd}:\text{ZnO}=5:100$ (weight ratio).

Examples 31, 32

- [0125] A catalyst was prepared according to the same method as Examples 29, 30, except that cerium oxide (guaranteed reagent, Kanto Kagaku) was used instead of zinc oxide.
- [0126] The composition of the obtained catalyst was $\text{Pd}:\text{CeO}_2=5:100$ (weight ratio).

Examples 33,34

- [0127] 6 ml hydrochloric acid and 8.33 g palladium chloride (PdCl_2) were dissolved in about 500 ml demineralized water, and 100 g zinc γ -alumina ("N612", Nikki Kagaku) was put in the aqueous solution, followed by evaporating to dryness. The matter was dried in air at 120 °C for 24 hours, and further sintered in air at 500 °C for 3 hours. Subsequently, this matter was put in an aqueous solution of 50 g sodium hydroxide dissolved in about 1,000 ml demineralized water, and treated at 50 °C with heating for about 1 hour. Then, it was separated without washing, and dried. Furthermore, this matter was graded to 20 to 40 mesh by compression molding, and treated in hydrogen current at 500 °C for 3 hours to obtain the catalyst.
- [0128] The composition of the obtained catalyst was $\text{Pd}:\text{Na}_2\text{O}:\text{Al}_2\text{O}_3=5:0.4:100$ (weight ratio).

Examples 35,36

- [0129] 6 ml hydrochloric acid and 8.33 g palladium chloride (PdCl_2) were dissolved in about 500 ml demineralized water, and 100 g silica gel ("ID", Fuji Davidson Kagaku) was put in the aqueous solution, followed by evaporating to dryness. The matter was dried in air at 120 °C for 24 hours, and further sintered in air at 500 °C for 3 hours. Subsequently, this matter was put in an aqueous solution of 10 g calcium hydroxide dissolved in about 1,000 ml demineralized water, and treated at 50 °C with heating for about 1 hour. Then, it was washed, followed by drying. Furthermore, about 80 g of this matter was put in an aqueous solution of 6.6 g calcium hydroxide dissolved in about 200 ml demineralized water, and evaporated to dryness, followed by drying. Furthermore, this matter was graded to 20 to 40 mesh by compression molding, and treated in hydrogen current at 500 °C for 3 hours to obtain the catalyst.
- [0130] The composition of the obtained catalyst was $\text{Pd}:\text{CaO}:\text{SiO}_2=5:5:100$ (weight ratio).

Reaction Method

- [0131] A prescribed amount of the above catalyst was packed in a stainless steel reaction tube having an inside diameter of 20 mm. A prescribed amount of dimethyl ether and water vapor and/or carbon dioxide were supplied to the reaction tube, and the reaction was carried out at a prescribed temperature.
- [0132] The reaction products and unreacted materials obtained by the above operations were analyzed by gas chromatography.

Reaction Conditions and Experimental Results

- [0133] The reaction conditions and experimental results are shown in Tables 10 and 11.

Table 10

		Example 29	Example 30	Example 31	Example 32
Catalyst (weight ratio)		Pd-ZnO (5:100)		Pd-CeO ₂ (5:100)	
Reaction Conditions	Temperature (°C)	300	350	300	350
	H ₂ O/Dimethyl Ether (Molar Ratio)	5	0	5	0
	CO ₂ /Dimethyl Ether (Molar Ratio)	0	1	0	1
	Space Velocity (h ⁻¹)	12000	7000	12000	7000
Results of Reaction	DME Conversion Rate (%)	99.7	89.4	91.4	90.2
	Yield (%)	Synthesis Gas	93.6	87.2	83.4
		Methanol	0.2	0	0.3
		Hydrocarbons	2.8	2.2	3.3
		CO ₂	3.1	—	4.4
	H ₂ /CO in Synthesis Gas (Molar Ratio)	2.46	0.95	2.20	0.84

Table 11

		Example 33	Example 34	Example 35	Example 36
Catalyst (weight ratio)		Pd-Na ₂ O-Al ₂ O ₃ (5:0.4:100)		Pd-CaO-SiO ₂ (5:5:100)	
Reaction Conditions	Temperature (°C)	300	350	300	350
	H ₂ O/Dimethyl Ether (Molar Ratio)	5	0	5	0
	CO ₂ /Dimethyl Ether (Molar Ratio)	0	1	0	1
	Space Velocity (h ⁻¹)	12000	7000	12000	7000
Results of Reaction	DME Conversion Rate (%)	88.9	84.9	95.1	73.8
	Yield (%)	Synthesis Gas	79.5	83.7	86.1
		Methanol	0.1	0	0.1
		Hydrocarbons	4.1	1.2	5.1
		CO ₂	5.2	—	3.8
	H ₂ /CO in Synthesis Gas (Molar Ratio)	2.38	0.88	2.51	0.89

EP 0 978 314 A1

Examples 37 - 42

[0134] 0.777 g iridium chloride (IrCl_3) was dissolved in about 300 ml demineralized water, and furthermore, 99.5 g γ -alumina ("AlO-4", Shokubai Gakkai) was put in the aqueous solution, followed by evaporating to dryness. The matter was dried in air at 120 °C for 24 hours, and sintered at 500 °C for 3 hour in air. Subsequently, it was treated in hydrogen current at 500 °C for 3 hours to obtain the catalyst.

[0135] The composition of the obtained catalyst was $\text{Ir}:\text{Al}_2\text{O}_3=0.5:99.5$ (weight ratio).

Reaction Method

[0136] A prescribed amount of the above catalyst was packed in a stainless steel reaction tube having an inside diameter of 20 mm. A prescribed amount of dimethyl ether and water vapor were supplied to the reaction tube, and the reaction was carried out at a prescribed temperature.

[0137] The reaction products and unreacted materials obtained by the above operations were analyzed by gas chromatography.

Reaction Conditions and Experimental Results

[0138] The reaction conditions and experimental results are shown in Tables 12 and 13.

Table 12

		Example 37	Example 38	Example 39	
Catalyst (weight ratio)		Ir-Al ₂ O ₃ (0.5:99.5)			
Conditions	Temperature (°C)	350	400	450	
	H ₂ O/Dimethyl Ether (Molar Ratio)	1	1	1	
	Space Velocity (h ⁻¹)	10000	10000	10000	
Results of Reaction	DME Conversion Rate (%)		18.7	40.2	98.7
	Yield (%)	Synthesis Gas	4.7	14.5	73.0
		Methanol	14.0	13.7	2.9
		Hydrocarbons	0	12.1	22.8
		CO ₂	0	0	0

Table 13

		Example 40	Example 41	Example 42	
Catalyst (weight ratio)		Ir-Al ₂ O ₃ (0.5:99.5)			
Conditions	Temperature (°C)		450	450	450
	H ₂ O/Dimethyl Ether (Molar Ratio)		3	5	10
	Space Velocity (h ⁻¹)		10000	10000	10000
Results of Reaction	DME Conversion Rate (%)		98.0	97.3	99.5
	Yield (%)	Synthesis Gas	83.2	89.5	95.6
		Methanol	1.1	0.3	0.2
		Hydrocarbons	13.7	7.5	3.7
		CO ₂	0	0	0

Examples 43-48

[0139] 0.863 g platinum chloride (PtCl_4) was dissolved in about 300 ml 10 wt. % hydrochloric acid aqueous solution, and furthermore, 99.5 g γ -alumina ("ALO-4", Shokubai Gakkai) was put in the aqueous solution, followed by evaporating to dryness. The matter was dried in air at 120 °C for 24 hours, and sintered at 500 °C for 3 hour in air. Subsequently, it was treated in hydrogen current at 500 °C for 3 hours to obtain the catalyst.

[0140] The composition of the obtained catalyst was $\text{Pt}:\text{Al}_2\text{O}_3=0.5:99.5$ (weight ratio).

Reaction Method

[0141] A prescribed amount of the above catalyst was packed in a stainless steel reaction tube having an inside diameter of 20 mm. A prescribed amount of dimethyl ether and water vapor were supplied to the reaction tube, and the reaction was carried out at a prescribed temperature.

[0142] The reaction products and unreacted materials obtained by the above operations were analyzed by gas chromatography.

Reaction Conditions and Experimental Results

[0143] The reaction conditions and experimental results are shown in Tables 14 and 15.

Table 14

		Example 43	Example 44	Example 45
Catalyst (weight ratio)		Pt-Al ₂ O ₃ (0.5:99.5)		
Conditions	Temperature (°C)	300	350	400
	H ₂ O/Dimethyl Ether (Molar Ratio)	1	1	1
	Space Velocity (h ⁻¹)	10000	10000	10000
Results of Reaction	DME Conversion Rate (%)		21.6	40.2
	Yield (%)	Synthesis Gas	7.1	19.3
		Methanol	9.3	11.7
		Hydrocarbons	2.2	12.5
		CO ₂	3.0	0

Table 15

		Example 46	Example 47	Example 48
Catalyst (weight ratio)		Pt-Al ₂ O ₃ (0.5:99.5)		
Conditions	Temperature (°C)	400	400	400
	H ₂ O/Dimethyl Ether (Molar Ratio)	3	5	10
	Space Velocity (h ⁻¹)	10000	10000	10000
Results of Reaction	DME Conversion Rate (%)		96.6	95.9
	Yield (%)	Synthesis Gas	74.1	79.4
		Methanol	18.7	11.4
		Hydrocarbons	0	0
		CO ₂	3.8	5.1

Examples 49-54

[0144] 1.40 g rhodium nitrate ($\text{Rh}(\text{NO}_3)_3$) was dissolved in about 300 ml demineralized water, and furthermore, 99.5 g γ -alumina ("ALO-4", Shokubai Gakkai) was put in the aqueous solution, followed by evaporating to dryness. The material was dried in air at 120 °C for 24 hours, and sintered at 500 °C for 3 hours in air. Subsequently, it was treated in hydrogen current at 500 °C for 3 hours to obtain the catalyst.

[0145] The composition of the obtained catalyst was $\text{Rh}:\text{Al}_2\text{O}_3=0.5:99.5$ (weight ratio).

Reaction Method

[0146] A prescribed amount of the above catalyst was packed in a stainless steel reaction tube having an inside diameter of 20 mm. A prescribed amount of dimethyl ether and water vapor dioxide were supplied to the reaction tube, and the reaction was carried out at a prescribed temperature.

[0147] The reaction products and unreacted materials obtained by the above operations were analyzed by gas chromatography.

Reaction conditions and Experimental Results

[0148] The reaction conditions and experimental results are shown in Tables 16 and 17.

Table 16

		Example 49	Example 50	Example 51	
Catalyst (weight ratio)		Rh-Al ₂ O ₃ (0.5:99.5)			
Conditions	Temperature (°C)	350	400	450	
	H ₂ O/Dimethyl Ether (Molar Ratio)	1	1	1	
	Space Velocity (h ⁻¹)	10000	10000	10000	
Results of Reaction	DME Conversion Rate (%)		19.1	65.3	89.7
	Yield (%)	Synthesis Gas	7.4	40.5	65.5
		Methanol	11.7	7.2	1.8
		Hydrocarbons	0	17.6	22.4
		CO ₂	0	0	0

Table 17

		Example 52	Example 53	Example 54	
Catalyst (weight ratio)		Rh-Al ₂ O ₃ (0.5:99.5)			
Conditions	Temperature (°C)	400	400	400	
	H ₂ O/Dimethyl Ether (Molar Ratio)	3	5	10	
	Space Velocity (h ⁻¹)	10000	10000	10000	
Results of Reaction	DME Conversion Rate (%)		72.1	88.6	90.9
	Yield (%)	Synthesis Gas	57.0	76.5	78.7
		Methanol	3.1	1.3	0.5
		Hydrocarbons	10.5	7.0	2.8
		CO ₂	1.5	3.8	8.9

Examples 55-56

[0149] 0.833 g palladium chloride (PdCl_2) was dissolved in 5 ml hydrochloric acid, and the volume was made about 500 ml by adding demineralized water. 99.5 g silica gel ("SIO-2", Shokubai Gakkai) was put in the aqueous solution, followed by evaporating to dryness. The matter was dried in air at 120 °C for 24 hours, and sintered at 500 °C for 3 hours in air. Subsequently, after grading to 20 to 40 mesh, it was treated in hydrogen current at 500 °C for 3 hours. The composition of this matter $\text{Pd}:\text{Al}_2\text{O}_3=0.5:99.5$ (weight ratio). γ -alumina ("ALO-4", Shokubai Gakkai) graded to 20 to 40 mesh was mixed physically with this matter at a ratio by weight of 1:1 to obtain the catalyst.

Examples 60-64

[0150] 0.833 g palladium chloride (PdCl_2) was dissolved in 5 ml hydrochloric acid, and the volume was made about 500 ml by adding demineralized water. 98.5 g silica gel ("SIO-4", Shokubai Gakkai) was put in the aqueous solution, followed by evaporating to dryness. The matter was dried in air at 120 °C for 24 hours, and sintered in air at 500 °C for 3 hours. Subsequently, the matter was put in an aqueous solution of 1.46 g potassium carbonate (K_2CO_3) dissolved in about 500 ml demineralized water, and evaporated to dryness. Then, the matter was dried in air at 120 °C for 24 hours, and sintered in air at 500 °C for 3 hours. Furthermore, after grading to 20 to 40 mesh, it was treated in hydrogen current at 500 °C for 3 hours. The composition of this matter was $\text{Pd}:\text{K}_2\text{O}:\text{Al}_2\text{O}_3=0.5:1.0:98.5$ (weight ratio). γ -alumina ("ALO-4", Shokubai Gakkai) graded to 20 to 40 mesh was mixed physically with this matter at a ratio by weight of 1:1 to obtain the catalyst.

Examples 65-69

[0151] A catalyst was prepared according to the same method as Examples 55-59, except that titania ("TIO-4", Shokubai Gakkai) was used instead of silica gel.

Reaction Method

[0152] A prescribed amount of the above catalyst was packed in a stainless steel reaction tube having an inside diameter of 20 mm. A prescribed amount of dimethyl ether and water vapor and/or carbon dioxide were supplied to the reaction tube, and the reaction was carried out at a prescribed temperature.

[0153] The reaction products and unreacted materials obtained by the above operations were analyzed by gas chromatography.

Reaction Conditions and Experimental Results

[0154] The reaction conditions and experimental results are shown in Tables 18 to 20.

Table 18

		Example 55	Example 56	Example 57	Example 58	Example 59
Catalyst (weight ratio)		Pd/SiO ₂ +Al ₂ O ₃ ((0.5:99.5):100)				
Conditions	Temperature (°C)	350	400	450	400	400
	H ₂ O/Dimethyl Ether (Molar Ratio)	1	1	1	5	10
	Space Velocity (h ⁻¹)	10000	10000	10000	10000	10000
Results of Reaction	DME Conversion Rate (%)	40.6	81.6	95.6	93.7	97.3
	Yield (%)	Synthesis Gas	22.7	48.1	40.2	81.5
		Methanol	8.5	3.3	1.9	0.3
		Hydrocarbons	9.3	30.2	53.5	10.7
		CO ₂	0	0	0	1.2

Table 19

		Example 60	Example 61	Example 62	Example 63	Example 64
Catalyst (weight ratio)		Pd-K ₂ O/SiO ₂ +Al ₂ O ₃ ((0.5:1.0:98.5):100)				
Conditions	Temperature (°C)	350	400	450	400	400
	H ₂ O/Dimethyl Ether (Molar Ratio)	1	1	1	5	10
	Space Velocity (h ⁻¹)	10000	10000	10000	10000	10000
Results of Reaction	DME Conversion Rate (%)	28.0	24.4	40.9	48.6	76.9
	Yield (%)	Synthesis Gas	4.5	5.6	8.2	42.1
		Methanol	23.5	18.1	7.8	5.5
		Hydrocarbons	0	0.7	24.9	0.1
		CO ₂	0	0	0	0.4

Table 20

		Example 65	Example 66	Example 67	Example 68	Example 69
Catalyst (weight ratio)		Pd-TiO ₂ +Al ₂ O ₃ ((0.5:99.5):100)				
Conditions	Temperature (°C)	350	400	450	400	400
	H ₂ O/Dimethyl Ether (Molar Ratio)	1	1	1	5	10
	Space Velocity (h ⁻¹)	10000	10000	10000	10000	10000
Results of Reaction	DME Conversion Rate (%)	23.4	29.5	46.8	69.9	83.5
	Yield (%)	Synthesis Gas	11.5	17.4	15.9	60.2
		Methanol	2.8	8.0	12.6	4.6
		Hydrocarbons	5.9	2.1	16.8	1.6
		CO ₂	3.3	2.1	1.4	3.5

Examples 70-72

[0155] 24.8 g nickel nitrate (Ni(NO₃)₂ · 6H₂O) was dissolved in about 300 ml demineralized water, and furthermore, 95 g γ - alumina ("ALO-4", Shokubai Gakkai) was put in the aqueous solution, followed by evaporating to dryness. The matter was dried in air at 120 °C for 24 hours, and sintered at 500 °C for 3 hour in air. Subsequently, it was treated in hydrogen current at 500 °C for 3 hours to obtain the catalyst.

[0156] The composition of the obtained catalyst was Ni:Al₂O₃=5:95 (weight ratio).

Examples 73-75

[0157] 32.1 g nickel nitrate (Ni(NO₃)₂ · 6H₂O) was dissolved in about 300 ml demineralized water, and furthermore, 90 g γ - alumina ("ALO-4", Shokubai Gakkai) was put in the aqueous solution, followed by evaporating to dryness. The matter was dried in air at 120 °C for 24 hours, and sintered at 500 °C for 3 hour in air. Subsequently, it was treated in a mixed gas current of hydrogen sulfide and hydrogen at a molar ratio of 1:1 at 500 °C for 3 hours to obtain the catalyst.

[0158] The composition of the obtained catalyst was NiS:Al₂O₃=10:90 (weight ratio).

Reaction Method

[0159] A prescribed amount of the above catalyst was packed in a stainless steel reaction tube having an inside diameter of 20 mm. A prescribed amount of dimethyl ether and water vapor were supplied to the reaction tube, and the reaction was carried out at a prescribed temperature.

[0160] The reaction products and unreacted materials obtained by the above operations were analyzed by gas chromatography.

Reaction Conditions and Experimental Results

[0161] The reaction conditions and experimental results are shown in Tables 21 and 22.

Table 21

		Example 70	Example 71	Example 72
Catalyst (weight ratio)		Ni-Al ₂ O ₃ (5:95)		
Conditions	Temperature (°C)	350	400	450
	H ₂ O/Dimethyl Ether (Molar Ratio)	1	1	1
	Space Velocity (h ⁻¹)	10000	10000	10000
Results of Reaction	DME Conversion Rate (%)	31.4	69.7	91.0
	Yield (%)	Synthesis Gas	17.6	41.8
		Methanol	10.0	5.6
		Hydrocarbons	3.8	22.3
		CO ₂	1.5	3.2

Table 22

		Example 73	Example 74	Example 75
Catalyst (weight ratio)		NiS-Al ₂ O ₃ (10:90)		
Conditions	Temperature (°C)	350	400	450
	H ₂ O/Dimethyl Ether (Molar Ratio)	1	1	1
	Space Velocity (h ⁻¹)	10000	10000	10000
Results of Reaction	DME Conversion Rate (%)	36.9	71.2	93.5
	Yield (%)	Synthesis Gas	27.0	65.5
		Methanol	9.1	4.2
		Hydrocarbons	0.8	1.5
		CO ₂	0	0

Example 76

[0162] Using a cathode base plate made of porous lanthanum calcium manganite $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$, a solid electrolyte membrane of stabilized zirconia 8 mol % $\text{Y}_2\text{O}_3\text{-ZrO}_2$ was formed on the base plate, and a platinum anode was provided on the electrolyte membrane to complete a solid electrolyte-type fuel cell. The fuel cell was operated at 1,000 °C, and a mixed gas of 4.7 % dimethyl ether, 2.6 % water vapor, the remainder Ar gas was directly supplied to be anode, and oxygen was supplied to the cathode as the oxidizing agent gas. Both electrodes were connected through a galvanostat, and electricity generation characteristics were investigated. As a comparison, hydrogen, which is ordinarily used, was supplied to the anode instead of the mixed gas, and electricity generation characteristics thereof were also investigated.

[0163] The results are shown in Figure 3. In the figure, \blacklozenge is dimethyl ether (voltage), \blacksquare is hydrogen (voltage), \diamond is dimethyl ether (generated electric power), and \square is hydrogen (generated electric power), respectively.

[0164] It can be seen that, even by supplying dimethyl ether and water vapor directly to the anode, electricity generation can be conducted to the degree of no problem as a solid electrolyte-type fuel cell, although electric generation efficiency is slightly inferior to the case of hydrogen. Moreover, problems of electrode deterioration and the like did not occur.

Example 77

[0165] Figure 4 is a flow sheet illustrating an example of the electricity generation method using the dimethyl ether reformed gas of the invention.

[0166] In a sintering machine cooler 11, sintered ore was air-cooled, the exhaust gas at 200 to 500 °C generated there was delivered to a heat exchanger 12 for heating water, a heat exchanger 13 for heating raw material gas and a heat exchanger 14 for heating heating medium. The heating medium heated by the sensible heat of the exhaust gas of the sintering machine cooler 11, is delivered to a dimethyl ether reformer 15. At the apparatus, a mixed gas consisting of dimethyl ether, steam and carbon dioxide gas, which has been previously heated by the sintering machine exhaust gas, is introduced into a plurality of reaction tubes arranged in the reformer 15. The inside of the reaction tubes is packed with dimethyl ether reforming catalyst, and by contacting the mixed gas consisting of dimethyl ether, steam and carbon dioxide gas with the catalyst, a mixed gas of carbon monoxide and hydrogen is produced. The inside temperature of the reformed 15 is, in general, in the temperature range of 200 to 500 °C, although it varies according to the type of the catalyst to be packed. The produced reformed gas contains a small amount of unreacted dimethyl ether. However, dimethyl ether itself is fuel gas having a great calorific value, and accordingly, the reformer gas containing dimethyl ether has no problem as the fuel for the combustor 16 for gas turbine. The obtained reformed gas is delivered to the combustor 16, and burns by the air for combustion supplied from a compressor 17. The exhaust gas generated in the combustor 16 is delivered to the gas turbine 18, and rotates an electricity generator 19 to generate electricity. The gas discharged from the gas turbine 18 is delivered to a gas turbine heat recovering boiler 20. The steam obtained in the gas turbine heat recovering boiler 20 is utilized as process steam in an iron manufacturing factory (not illustrated).

Generation Examples 1-4 and Comparative Generation Example

[0167] Using the dimethyl ether reformed gas obtained in a prescribed catalyst example, electricity generation tests were carried out by a simple open type gas turbine.

Table 23

Condition		Generation Example 1	Generation Example 2	Generation Example 3	Generation Example 4	Comparative Generation
	Reformed Gas	Example 2	Example 5	Example 10	Example 27	Comparative Reaction
	Reformed Gas Temp. (°C)	337	334	329	342	320
	Exhaust Gas Temp. (°C)	570	561	547	584	530
Results	Generating Efficiency (%)	44.6	44.3	43.6	45.8	41.5

Table 24

			Comparative Reaction
Catalyst (wt. ratio)			CuO-ZnO-Al ₂ O ₃ (30:20:50)
Conditions	Temperature (°C)		360
	H ₂ O/Methanol (Molar Ratio)		2
	Space Velocity (h ⁻¹)		15000
Results of Reaction	Methanol Conversion Rate (%)		84.2
	Yield (%)	Hydrogen	73.9
		CO ₂	21.5
		CO	4.6

Example 78

[0168] Figure 5 is a flow sheet illustrating an example of the reducing method of iron ore using the dimethyl ether reformed gas of the invention.

[0169] Dimethyl ether is previously heated at an heat exchanger 21 by the exhaust gas at 200 to 500 °C after reducing iron ore, furthermore, mixed with the exhaust gas comprising mainly steam and carbon dioxide gas after reducing iron ore supplied by a blower 22, and then, delivered to a dimethyl ether reformer 23. At the reformer 23, dimethyl ether

reforming catalyst is packed in a plurality of reaction tubes arranged therein, and the exhaust gas after reducing iron ore is introduced to the outside of the reaction tubes for supplying heat for endothermic reaction. By contacting the mixed gas consisting of dimethyl ether the exhaust gas after reducing iron ore with the catalyst in the reaction tubes, reformed gas comprising mainly carbon monoxide and hydrogen is produced. The inside temperature of the reformer 23 is, in general, in the temperature range of 200 to 500 °C, although it varies according to the type of the catalyst to be packed. The obtained reformed gas is delivered is a heating furnace 24 to raise its temperature to 800 to 1000 °C, and introduced into a reducing furnace 25. At the reducing furnace 25, iron ore is loaded from the upper part, and the iron ore is reduced by the reformed gas introduced from the middle bottom part, and the reduced iron is discharged from the under part.

Reduction Examples 1-6

[0170] A prescribed amount of iron ore pellets or clump ore having a grain diameter of 5 to 10 mm was loaded in a shaft-type reducing furnace. The dimethyl ether reformed gas obtained in a prescribed catalyst example was heated to a prescribed temperature, and a prescribed amount was streamed for a prescribed time to reduce iron ore.

Table 25

Raw Material	Ore	Reduction Example 1	Reduction Example 2	Reduction Example 3	Reduction Example 4	Reduction Example 5	Reduction Example 6
		Pellet	Clump Ore	Pellet	Pellet	Pellet	Pellet
	Loaded Amount (kg)	1	1	1	1	1	1
Conditions	Reformed Gas	Catalyst Example 5	Catalyst Example 5	Catalyst Example 10	Catalyst Example 27	Catalyst Example 5	Catalyst Example 5
	Reformed Gas Flow Rate (Nm ³ /h)	4	4	3	6	5	3
	Inlet Temp. (°C)	900	900	850	950	850	950
	Pressure (atm)	1	1	1	1	1	1
	Time (h)	3	3	2	3	2	3
Results	Metallized Rate (%)	92	92	94	93	91	91

Industrial Applicability

[0171] The catalyst of the invention can obtain hydrogen or synthesis gas in a high yield by reaction dimethyl ether and water vapor or carbon dioxide at a low temperature of 150 to 600 °C. The hydrogen obtained in the invention has wide applications as various raw materials, and is useful for fuel cell, fuel for electricity generation, reduction of iron ore, etc.

Claims

1. A catalyst for producing hydrogen gas from a mixed gas comprising dimethyl ether and water vapor or carbon dioxide gas, which comprises copper, iron, cobalt, palladium, iridium, platinum, rhodium, or nickel as an active compo-

nent.

2. The catalyst as set forth in claim 1 wherein, the active component is copper or iron, the mixed gas comprises dimethyl ether and carbon dioxide gas, and the produced gas is synthetic gas.
3. The catalyst as set forth in claim 1 wherein, the active component is cobalt, palladium, iridium, platinum, rhodium or nickel, the mixed gas comprises dimethyl ether and water vapor, and the produced gas is synthesis gas.
4. The catalyst as set forth in claim 1 wherein, the active component is copper or iron, the mixed gas comprises dimethyl ether and water vapor, and the produced gas comprises hydrogen as a principal component.
5. The catalyst as set forth in claim 1 wherein, the active component is cobalt or palladium carried by a metal oxide having basicity, and the produced gas is synthesis gas.
6. The catalyst as set forth in claim 1 wherein, the active component is platinum, the mixed gas comprises dimethyl ether and water vapor, and the produced gas is synthesis gas.
7. A method of producing hydrogen gas which comprises contacting a mixed gas comprising dimethyl ether and water vapor or carbon dioxide gas with a catalyst as set forth in claim 1.
8. A method of producing synthesis gas wherein, the mixed gas comprises dimethyl ether and carbon dioxide gas, and the catalyst is as set forth in claim 2.
9. A method of producing synthesis gas wherein, the mixed gas comprises dimethyl ether and water vapor, and the catalyst is as set forth in claim 3.
10. A method of producing water vapor wherein, the mixed gas comprises dimethyl ether and water vapor, and the catalyst is as set forth in claim 4.
11. A fuel cell using dimethyl ether as the fuel and a catalyst as set forth in claim 1.
12. A solid electrolyte-type fuel cell using a mixed gas comprising dimethyl ether and water vapor as fuel gas and a catalyst as set forth in claim 1.
13. As electricity generation method using dimethyl ether reformed gas which comprises reforming dimethyl ether to produce synthesis gas or hydrogen gas by adding water vapor or carbon dioxide gas to the dimethyl ether and catalyzing them using a catalyst as set forth in claim 1, and using the produced gas as a fuel for engine.
14. The electricity generation method as set forth in claim 13 which comprises reforming dimethyl ether utilizing medium, low temperature waste heat in the range of 200 to 500 °C.
15. An electricity generating apparatus which comprises a reformer loaded with a catalyst as set forth in claim 1, a combustor for burning the synthesis gas or hydrogen gas, and an electricity generator having gas turbine rotated by the combustion exhaust gas generated in the combustor.
16. A method of manufacturing reduced iron which comprises reforming dimethyl ether to produce synthesis gas or hydrogen gas by adding water vapor or carbon dioxide gas to the dimethyl ether and catalyzing them using a catalyst as set forth in claim 1, and reducing iron are using the produced gas.
17. The method of manufacturing reduced iron as set forth in claim 16 wherein the reforming of dimethyl ether is carried out using an exhaust gas containing water vapor and carbon dioxide gas obtained by reducing the iron are.
18. The method of manufacturing reduced iron as set forth in claim 16 or 17 wherein sensible heat of the exhaust gas obtained by reducing the iron are is utilized as a heating source of the dimethyl ether reforming.
19. A manufacturing apparatus of reduced iron which comprises a reformer loaded with a catalyst as set forth in claim 1, and a reducing furnace loaded with iron ore, and the reducing furnace being connected with the reformer so that synthesis gas or hydrogen gas produced in the reformer is supplied to the reducing furnace.

Fig. 1

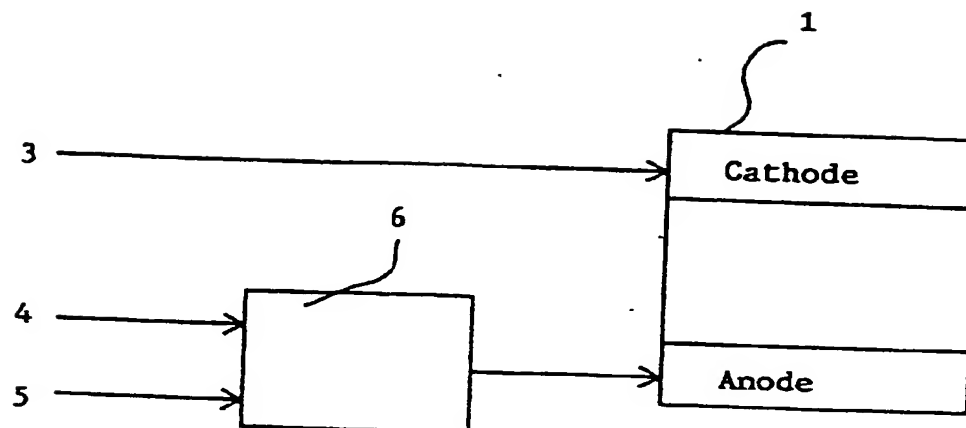


Fig. 2

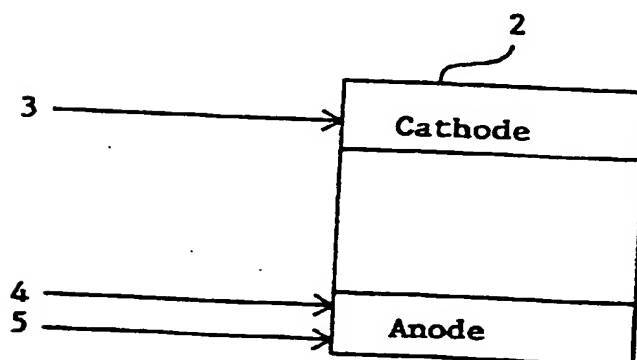


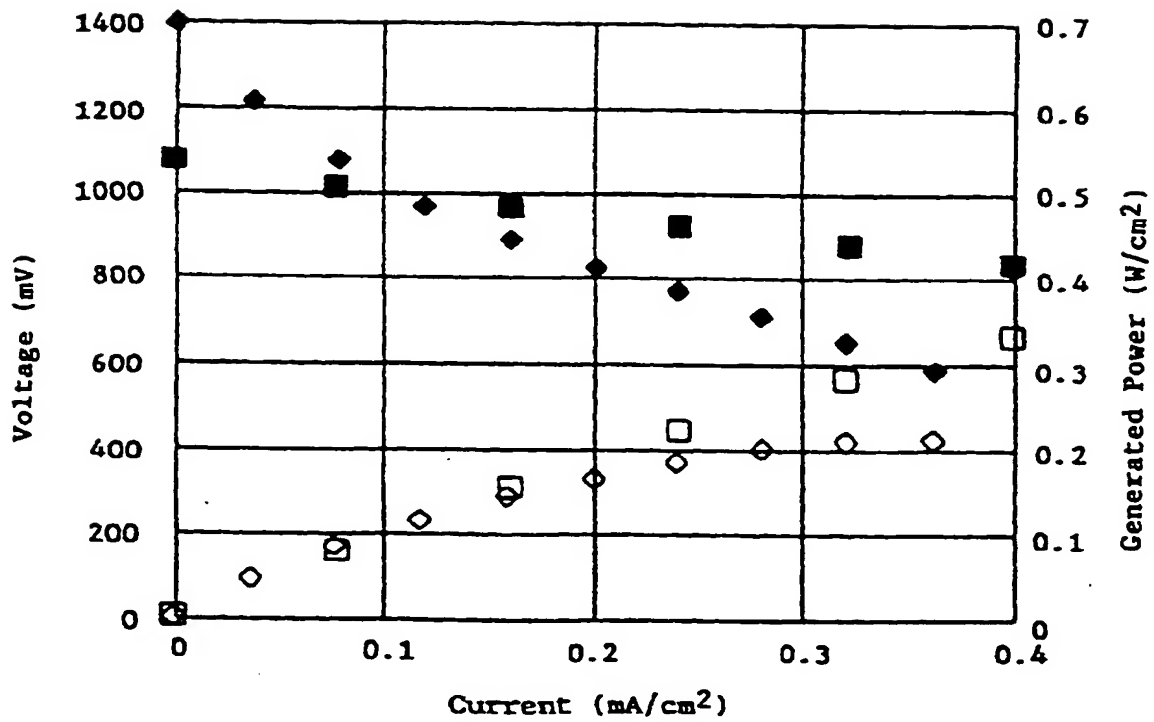
Fig. 3

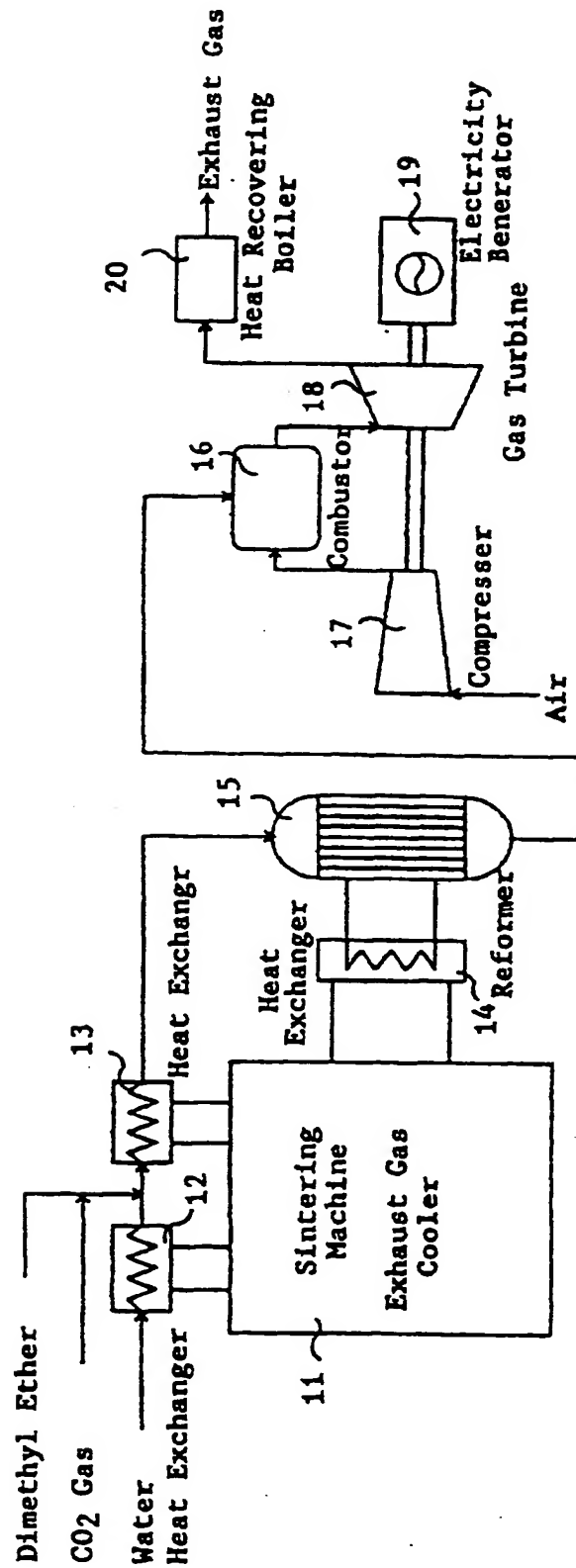
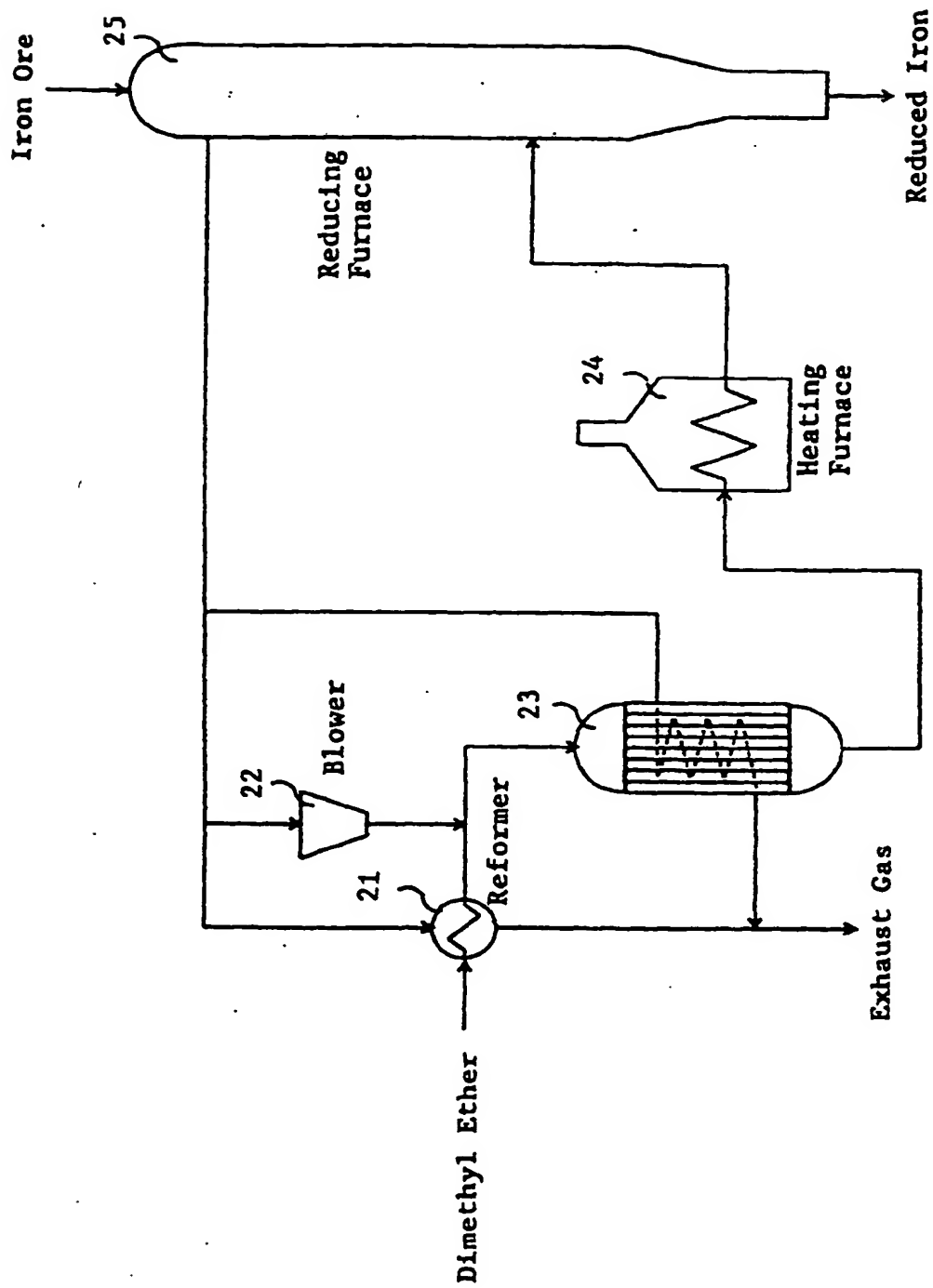
Fig. 4

Fig. 5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/02640

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl.⁶ B01J23/40, B01J23/70, C01B3/38, C22B5/12, F02C6/00, H01M8/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl.⁶ B01J23/40, B01J23/70, C01B3/38, C22B5/12, F02C6/00, H01M8/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1926-1996	Toroku Jitsuyo Shinan Koho	1994-1998
Kokai Jitsuyo Shinan Koho	1971-1998	Jitsuyo Shinan Keisai Koho	1996-1998

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP, 3-14761, B (Imperial Chemical Industries PLC.), 27 February, 1991 (27. 02. 91), Page 2, column 4, line 37 to page 3, column 5, line 10 ; page 4, column 8, lines 9 to 14 ; Page 6, column 11, line 2 to column 12, line 15 ; page 4, column 8, lines 24 to 29 & GB, 2085314, A	1-10 16-19
X	WO, 96/18573, A (Amoco Corp.), 20 June, 1996 (20. 06. 96), Full text	1-4, 7-10, 13-15
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☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search
8 September, 1998 (08. 09. 98)Date of mailing of the international search report
29 September, 1998 (29. 09. 98)Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/02640

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Microfilm of the specification and drawings annexed to the request of Japanese Utility Model Application No. 50266/1983 (Laid-open No. 176950/1983) (Mitsubishi Heavy Industries, Ltd.), 26 November, 1983 (26. 11. 83), Claims ; page 9, lines 3 to 10 ; Fig. 2 (Family: none)	16-19
X	JP, 1-148343, A (Shin Gijutsu Kaihatsu Jigyodan), 9 June, 1989 (09. 06. 89), Claims (Family: none)	1-6
EX	JP, 10-177864, A (Toshiba Corp.), 30 June, 1998 (30. 06. 98), Claims ; page 9, column 9, line 43 to page 10, column 17, line 10, column 18, lines 40 to 45 (Family: none)	1-4, 6-12
EX	JP, 10-189022, A (NKK Corp.), 21 July, 1998 (21. 07. 98), Claims ; page 2, column 2, line 46 to page 3, column 3, lines 3, 8 to 14 (Family: none)	1, 3, 6, 7, 9, 11, 12
EX	JP, 10-174865, A (NKK Corp.), 30 June, 1998 (30. 06. 98), Claims ; page 2, column 2, lines 35 to 46 (Family: none)	1, 3, 5, 7, 9
EX	JP, 10-174871, A (NKK Corp.), 30 June, 1998 (30. 06. 98), Claims ; page 2, column 2, lines 11 to 31 (Family: none)	1, 3, 5, 7, 8
EX	JP, 10-174873, A (NKK Corp.), 30 June, 1998 (30. 06. 98), Claims ; page 2, column 2, lines 5 to 24 (Family: none)	1, 2, 4, 7, 10
EX	JP, 10-174870, A (NKK Corp.), 30 June, 1998 (30. 06. 98), Claims ; page 2, column 2, lines 5 to 24 (Family: none)	1, 2, 4, 7, 10
EX	JP, 10-174865, A (NKK Corp.), 30 June, 1998 (30. 06. 98), Claims ; page 2, column 2, lines 9 to 28 (Family: none)	1, 2, 4, 7, 8, 10

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/02640

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Since the catalyst disclosed in Claim 1 is known in the art, there is no technical relationship involving any specific technical features between the invention disclosed in Claim 1 and the inventions disclosed in Claims 11, 13, 15, 16 and 19. Therefore, Claims 11, 13, 15, 16 and 19 are not considered as fulfilling the requirement of unity of invention.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
 2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
 3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
 4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
- Remark on Protest** ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

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